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IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re the accompanying application of )  
CAROLUS M. A. M. MESTERS and )  
RONALD J. SCHOONEBEEK )  
Serial No. 10/738,332 )  
Filed December 17, 2003 )  
PROCESS FOR THE CATALYTIC )  
SELECTIVE OXIDATION OF SULFUR )  
COMPOUNDS )

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Sir:

**CLAIM TO PRIORITY**

Applicants reaffirm the claim for the benefit of filing date of the following foreign patent application referred to in Applicant's Declaration:

European application Serial No. 02258672.1 filed December 17, 2002

A copy of the application certified by the European Patent Office is enclosed.

Respectfully submitted,

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The attached documents  
are exact copies of the  
European patent application  
described on the following  
page, as originally filed.

Les documents fixés à  
cette attestation sont  
conformes à la version  
initialement déposée de  
la demande de brevet  
européen spécifiée à la  
page suivante.

**Patentanmeldung Nr.    Patent application No.    Demande de brevet n°**

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Der Präsident des Europäischen Patentamts;  
Im Auftrag

For the President of the European Patent Office

Le Président de l'Office européen des brevets  
p.o.

**R C van Dijk**





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Anmelder/Applicant(s)/Demandeur(s):

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Bezeichnung der Erfindung/Title of the invention/Titre de l'invention:  
(Falls die Bezeichnung der Erfindung nicht angegeben ist, siehe Beschreibung.  
If no title is shown please refer to the description.  
Si aucun titre n'est indiqué se référer à la description.)

Process for the catalytic selective oxidation of sulphur compounds.

In Anspruch genommene Priorität(en) / Priority(ies) claimed /Priorité(s)  
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PROCESS FOR THE CATALYTIC SELECTIVE OXIDATION OF SULPHUR  
COMPOUNDS

The present invention relates to a process for the catalytic selective oxidation of sulphur compounds in a hydrocarbonaceous feedstock to sulphur dioxide.

5 Hydrocarbonaceous feedstock are usually desulphurised in a hydrodesulphurisation process. In this process, the sulphur containing feedstock is contacted with a hydrodesulphurisation catalysts, typically a Co-Mo or Ni-Mo catalyst, in the presence of hydrogen.

10 It is known to use catalysts comprising nickel, zinc oxide and alumina for deep desulphurisation of hydrocarbon streams, i.e. to sulphur concentrations as low as 0.1 ppm. These catalysts have a double function: nickel catalyses the reaction of sulphur with hydrogen to form hydrogen sulphide and zinc oxide absorbs the  
15 hydrogen sulphide formed. In WO 01/15804, for example, a catalyst is disclosed having 5-25 wt% Ni, 30-70 wt% ZnO and the remainder alumina.

20 It has now been found that sulphur in hydrocarbonaceous streams can be converted into sulphur dioxide by catalytic selective oxidation. The thus-formed sulphur dioxide can be removed by processes known in the art. Reference herein to selective oxidation of sulphur compounds is to the oxidation of sulphur compounds with no or minimal oxidation of the non-sulphur containing  
25 hydrocarbonaceous compounds. An advantage of selective oxidation followed by removal of sulphur dioxide is that no hydrogen is needed for the desulphurisation. Moreover,

for deep desulphurisation, catalysts without nickel, which is known to be toxic and carcinogenic, can be used.

Accordingly, the present invention relates to a process for the catalytic selective oxidation of sulphur compounds in a hydrocarbonaceous feedstock to sulphur dioxide, wherein a feed mixture of the hydrocarbonaceous feedstock and a molecular-oxygen containing gas is contacted with a catalyst, wherein the oxygen-to-carbon ratio of the feed mixture is below 0.15.

10 Sulphur compounds that can be selectively oxidised by the process according to the invention are for example hydrogen sulphide, mercaptans, or heterocyclic sulphur compounds such as thiophenes or benzothiophenes.

15 The hydrocarbonaceous feedstock preferably is a hydrocarbonaceous feedstock that is gaseous under the conditions prevailing at the catalyst surface. Preferred feedstocks are feedstocks that are gaseous at standard temperature and pressure (STP; 0 °C, 1 atm.) conditions such as methane, natural gas, LPG and other gaseous hydrocarbon streams. Feedstocks that are liquid under STP conditions but gaseous at the conditions prevailing at the catalyst surface such as naphtha, diesel or gasoline are also very suitable.

25 The catalyst of the process according to the invention comprises an oxidising solid surface, typically in the form of solid particles. Reference herein to an oxidising surface is to a surface that is able to activate molecular oxygen. Preferably, the catalyst comprises a refractory oxide. Refractory oxides such as stabilised and partially stabilised zirconia, ceria, yttria, silica, alumina, titania and combinations thereof are particularly suitable. A catalyst comprising stabilised or partially stabilised zirconia is most



preferred. Alternatively, the catalyst may comprise a non-refractory oxide bulk material having an oxidising surface. Examples of such materials are a Fe, Cr and Al containing alloy (commercialised as FECRALLOY) with an alumina or zirconia surface layer (FECRALLOY is a trademark).

Preferably, the catalyst comprises one or more catalytically active metals supported on the solid surface or carrier. Preferred catalytically active metals are noble metals, more preferably rhodium and iridium. The catalyst is preferably free of nickel.

Typically, the catalyst comprises the catalytically active metal(s) in a concentration in the range of from 0.02 to 10% by weight, based on the total weight of the catalyst, preferably in the range of from 0.1 to 5% by weight. The catalyst may further comprise a performance-enhancing inorganic metal cation selected from Al, Mg, Zr, Ti, La, Hf, Si, Ba, and Ce which is present in intimate association supported on or with the catalytically active metal, preferably a zirconium and/or cerium cation.

The preferred catalysts, i.e. catalysts comprising a noble metal on a carrier, are catalysts that are also suitable for the catalytic partial oxidation of hydrocarbons, typical at temperatures above 700 °C. It has been found that at much lower temperatures, typically between 250 and 500 °C, the oxidation of sulphur compounds takes preferentially place as compared to the oxidation of hydrocarbons. Therefore, the temperature of the catalyst is preferably maintained at a temperature in the range of from 250 to 500 °C if such catalysts are used.

If the catalyst in the process of the present invention is an oxidising surface without a catalytically active metal, the preferred operating temperature is higher, i.e. in the range of from 350 to 600 °C.

5       The molecular-oxygen containing gas may be oxygen, air or oxygen-enriched air. Preferably, air is used as molecular-oxygen containing gas.

10       It will be appreciated that the exact process conditions, such as the temperature at which the catalyst is maintained, pressure, gas or liquid velocity and the oxygen-to-carbon ratio in the feed mixture, will inter alia depend on the catalyst used and the required sulphur conversion and selectivity.

15       The oxygen-to-carbon ratio of the feed mixture is at most 0.15, preferably at most 0.10. Reference herein to the oxygen-to-carbon ratio is to the ratio of oxygen in the form of molecules ( $O_2$ ) to carbon atoms present in the hydrocarbonaceous feedstock.

20       The process according to the invention is particularly suitable for the removal of small amounts of sulphur from a hydrocarbonaceous stream, such as the removal of hydrogen disulphide from gaseous hydrocarbonaceous steams comprising up to 10% v/v hydrogen disulphide or the removal of sulphur compounds  
25       from liquid hydrocarbonaceous steams comprising up to 1000 ppmw sulphur.

30       The sulphur dioxide formed may be removed by techniques known in the art. In liquid feedstocks, sulphur dioxide may for example be removed by distillation or stripping. Suitable techniques known in the art for the removal of sulphur dioxide from gaseous feedstocks are for example solvent extraction using an aqueous amine solution or an alkaline solution,

absorption as sulphate on copper or barium oxide, or reaction with lime to produce gypsum.

In order to remove larger amounts of hydrogen sulphide from gaseous hydrocarbonaceous feedstocks, the selective oxidation process according to the invention can suitably be applied in combination with a process for the conversion of H<sub>2</sub>S/SO<sub>2</sub> mixtures into elemental sulphur according to the well-known Claus reaction:



Part of the hydrogen sulphide, preferably about one third of the total volumetric amount of hydrogen disulphide, is then converted into sulphur dioxide by the catalytic selective oxidation process according to the invention.

The process according to the invention will be further illustrated by the following non-limiting examples.

#### EXAMPLE 1

##### Catalyst preparation

##### Catalyst 1

Particles (1 mm average diameter) of zirconia partially stabilised with yttria (Y-PSZ) were coated with a zirconia paint (zirconium oxide partially-stabilised with 4 %wt CaO; type ZO; ex. ZYP Coatings Inc., Oak Ridge, USA) and provided with 0.9 wt% Rh, 0.9 wt% Ir, 0.6 wt% Zr, 1.9 wt% Ce by impregnating the painted particles with a solution containing rhodium tri chloride, iridium tetra chloride, zirconyl nitrate and cerium nitrate. The impregnated particles were dried at 140 °C during 2 hours and calcined at 700 °C during 2 hours.

#### Catalyst 2

Particles (1 mm average diameter) of zirconia partially stabilised with yttria (Y-PSZ) were coated with a zirconia paint (see above under catalyst 1) and provided with 0.5 wt% Zr, 1.6 wt% Ce by impregnating the painted particles with a solution containing zirconyl nitrate and cerium nitrate. The impregnated particles were dried at 140 °C during 2 hours and calcined at 700 °C during 2 hours.

#### Catalyst 3

Particles (30-80 mesh) of Y-PSZ were coated with a zirconia paint (see above under catalyst 1) and provided with 1.6 wt% Rh, 1.0 wt% Zr, 1.6 wt% Ce by impregnating the painted particles with a solution containing rhodium tri chloride, zirconyl nitrate and cerium nitrate. The impregnated particles were dried at 140 °C during 2 hours and calcined at 700 °C during 2 hours.

#### Catalyst 4

Particles (30-80 mesh) of zirconia-toughened alumina partially stabilised with ceria (Ce-ZTA) were impregnated with a solution containing  $\text{H}_2\text{PtCl}_6$  and zirconyl nitrate. The impregnated particles were dried at 140 °C during 2 hours and calcined at 700 °C during 2 hours. The resulting catalyst particles contained 5 wt% Pt and 7 wt% Zr.

#### Catalyst 5

Calcined (2 hours at 1000 °C) particles (30-80 mesh) of alumina stabilised with magnesium oxide were provided with 0.6 wt% Ir by impregnating the particles with a iridium tetra chloride containing solution. The impregnated particles were dried (2 hours at 120 °C) and calcined (2 hours at 700 °C).

### Catalyst 6

Particles (1 mm average diameter) Y-PSZ were coated with a zirconia paint and provided with 0.8 wt% Rh, 0.8 wt% Ir, 0.6 wt% Zr, 1.7 wt% Ce by impregnating the painted particles with a solution containing rhodium tri  
chloride, iridium tetra chloride, zirconyl nitrate and cerium nitrate. The impregnated particles were dried at 140 °C during 2 hours and calcined at 700 °C during 2 hours.

### Catalytic selective oxidation

Approximately 1 g of catalyst particles were loaded in a 6 mm inner diameter reactor tube. A gas mixture of air and H<sub>2</sub>S-containing methane was passed over the catalyst particles at elevated temperature and at ambient pressure.

In Table 1, the H<sub>2</sub>S concentration of the H<sub>2</sub>S-containing methane, the oxygen-to-carbon ratio of the air/methane mixture, the gas space velocity (Nl feed mixture per kg catalyst per hour), the temperature at which the catalyst is maintained, the H<sub>2</sub>S conversion and the selectivity are given for each catalyst. The selectivity is calculated as the quotient of the molar SO<sub>2</sub>/CO<sub>2</sub> ratio in the effluent and the S/C ratio in the feed.

Table 1 Selective oxidation of H<sub>2</sub>S in methane: feed composition,  
process conditions and results.

Catalyst No.	1		2		3	4	5	6
H <sub>2</sub> S (% v/v)	2.8	2.0	2.5	2.5	2.0	1.7	1.5	1.6
O <sub>2</sub> :C	0.06	0.04	0.05	0.05	0.05	0.07	0.05	0.06
GSV (Nl/kg/h)	7,000	7,000	7,000	7,000	7,000	7,000	13,000	7,000
T (°C)	360	459	413	553	470	458	467	433
H <sub>2</sub> S conversion (%)	99.9	99.7	73.7	99.9	97.1	94.7	95.2	96.7
selectivity	222	373	5070	8400	53	57	57	57

EXAMPLE 2

0.95 g of particles of catalyst 1 were loaded in a 6 mm inner diameter reactor tube. A gas mixture of air and thiophene-containing methane was passed over the catalyst particles at elevated temperature and ambient pressure. Two different experiments with different feed composition and different process conditions were carried out.

In Table 2, the sulphur concentration of the methane, the oxygen-to-carbon ratio of the air/methane mixture, the gas space velocity (Nl feed mixture per kg catalyst per hour), the temperature at which the catalyst is maintained, the thiophene conversion and the selectivity are given for the two experiments. The selectivity is calculated as the quotient of the molar SO<sub>2</sub>/CO<sub>2</sub> ratio in the effluent and the S/C ratio in the feed.

Table 2 Selective oxidation of thiophene in methane: feed composition, process conditions and results.

experiment	a	b
ppmw S	11,400	300
O <sub>2</sub> :C	0.05	0.02
GSV (Nl/kg/h)	8,000	7,000
T (°C)	391	304
thiophene conversion (%)	99.8	79.9
selectivity	28	1816

EXAMPLE 3

0.94 g of particles of catalyst 1 were loaded in a 6 mm inner diameter reactor tube. A mixture of air and thiophene-containing naphtha was passed over the catalyst particles at a temperature of 320 °C and ambient

pressure. The naphtha had a boiling range of 40-180 °C, a H/C ratio of 1.8, a density of 0.74 g/ml.

In Table 3, the sulphur concentration of the naphtha, the oxygen-to-carbon ratio of the air/naphtha mixture, the liquid space velocity (kg naphtha per kg catalyst per hour), the temperature at which the catalyst is maintained, the thiophene conversion and the selectivity are given. The selectivity is calculated as the quotient of the molar SO<sub>2</sub>/CO<sub>2</sub> ratio in the effluent and the S/C ratio in the feed.

Table 3 Selective oxidation of thiophene in naphtha: feed composition, process conditions and results.

ppmw S	590
O <sub>2</sub> :C	0.003
LSV (kg/kg/h)	23.4
T (°C)	320
thiophenes conversion (%)	62.7
selectivity	428



C L A I M S

1. A process for the catalytic selective oxidation of sulphur compounds in a hydrocarbonaceous feedstock to sulphur dioxide, wherein a feed mixture of the hydrocarbonaceous feedstock and a molecular-oxygen  
5 containing gas is contacted with a catalyst, wherein the oxygen-to-carbon ratio of the feed mixture is below 0.15.
2. A process according to claim 1, wherein the oxygen-to-carbon ratio of the feed mixture is below 0.10.
3. A process according to claim 1 or 2, wherein the  
10 catalyst comprises a refractory oxide.
4. A process according to claim 3, wherein the refractory oxide comprises partially stabilised or stabilised zirconia.
5. A process according to any one of the preceding  
15 claims, wherein the catalyst comprises a group VIII noble metal on a carrier, preferably Rh or Ir.
6. A process according to claim 5, wherein the catalyst is maintained at a temperature in the range of from 250 to 500 °C.
7. A process according to any one of claims 1 to 4,  
20 wherein the catalyst does not comprise a catalytic active metal and the catalyst is maintained at a temperature in the range of from 350 to 600 °C.
8. A process according to any one of the preceding  
25 claims, wherein the hydrocarbonaceous feedstock is a gaseous hydrocarbonaceous feedstock, more preferably methane or natural gas.
9. A process according to claim 8, wherein the hydrocarbonaceous feedstock comprises hydrogen sulphide

in a concentration of at most 10% v/v, preferably at most 5 % v/v.

10. A process according to any one of claims 1 to 7, wherein the feedstock is a liquid hydrocarbonaceous feedstock containing at most 1000 ppmw sulphur.

5

A B S T R A C T

PROCESS FOR THE CATALYTIC SELECTIVE OXIDATION OF SULPHUR  
COMPOUNDS

A process for the catalytic selective oxidation of sulphur compounds in a hydrocarbonaceous feedstock to sulphur dioxide, wherein a feed mixture of the hydrocarbonaceous feedstock and a molecular-oxygen containing gas is contacted with a catalyst, wherein the oxygen-to-carbon ratio of the feed mixture is below 0.15.

